Final Report

DEVELOPMENT OF
ELASTIC ELASTOMERIC FIBER

to

NATIONAL AERONAUTICS
AND SPACE ADMINISTRATION
MANNED SPACECRAFT CENTER
HOUSTON, TEXAS 77058

CONTRACT NO. 9-12815

ADL REFERENCE 74693

DATE: MARCH 1974

Arthur D. Little, Inc.

1972 — 1973

DEVELOPMENT OF ELASTIC ELASTOMERIC FIBER

by

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ACKNOWLEDGEMENT

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ABSTRACT

During 1972 and 1973, our efforts have been directed to improving the physical properties of and manufacturing techniques for the elastic elastomeric fluorinated polymer fiber developed previously. Strengths of 1200 psi to 2400 psi, double those previously reported for the fluorinated polymers have been attained without any sacrifice in elongation or flame retardancy. The fibers meet the 70% oxygen, 30% nitrogen at 6.2 psia flame resistant specification.

This improvement was achieved through the use of a new curing system based on peroxide and maleimide. The manufacturing process was improved by developing special techniques for extruding the uncured fiber into filaments. The process produces 24 monofilaments at one time. About 25 pounds of 15-denier fiber can now be produced per 8-hour day, and, if necessary, the production rate can be increased by scaling up the equipment.

Power net fabrics were prepared to meet the 70% O_2/30% N_2, 6.2 psia requirement. When a somewhat heavier fiber was used, these fabrics were equal in power to spandex. Recovery after repeated cycling was also very similar to that for spandex fibers. A variety of these experimental samples were wrapped with PBI, Nomex and glass fibers. The PBI-wrapped materials were selected for use in the construction of a number of sleep monitoring caps for simulated Skylab Medical Experiments tests. Tests on the elastic fiber as well as on the wrapped elastic fiber showed that the material has excellent aging and chemical resistance and meets the requirements for use in spacecraft in the 70/30 oxygen/nitrogen environment.

The strength can be improved further when the flammability requirement is reduced to a 30% oxygen atmosphere — as is permissible for certain uses — since less of the flame-retardant additive, which seriously weakens the fiber, can be used. The resulting fiber strength (4000 psi) is reasonably close to that of spandex fibers.

At present, an experimental program is under way, under a new contract, to utilize the technology developed and prepare different types of products including coated fabrics, foam, film and sheeting, and tubing.

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I. INTRODUCTION

The objective of this program has been to develop nonflammable elastomeric fibers for use in space suits and with certain equipment used by the crew of the spacecraft. The overall program was conducted under three different contracts:

Contract NAS 9-10424: Flame-retardant urethane polymers were synthesized and additives were incorporated in fluorinated and urethane polymers to impart flame retardancy. Compositions that were self-extinguishing in the 70% oxygen, 30% nitrogen atmosphere were made into fibers and incorporated into fabric structures where the elastic fibers were wrapped with nonelastic PBI, Nomex and Beta Fiberglas, to give nonflammable elastomeric structures.

Contract NAS 9-12815: The strength of the fibers was improved substantially and manufacturing techniques were refined. Quantities of fiber were prepared and power net fabrics were made that were satisfactory for sleep monitoring caps and other applications in the spacecraft.

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II. BACKGROUND

In the program for 1970-1971, which is covered in our report dated March 1971, various urethane-type polymers were synthesized, and many had better flame resistance than spandex. However, flame resistant fibers were produced most efficiently by incorporating halogenated additives into urethane or fluorocarbon elastomers. Some of the resultant fibers were not flammable even in a 100% oxygen environment.

Various flexible polyurethane structures containing halogen were synthesized from polyesters derived from aliphatic or aromatic polyols and dibasic acids. Aliphatic halide structures could not be used because they are unstable at the required reaction temperatures, giving off hydrogen halide which hydrolyzes the ester linkages. In contrast, halogen-containing aromatic polyols are stable and lead to satisfactory products.

The most promising composition, a brominated neopentyl glycol capped with toluene diisocyanate, was used as a conventional diisocyanate in conjunction with hydroxy-terminated polyethers or polyesters to form elastomeric urethanes containing about 10% bromine by weight. Products made in this manner will not burn in air, have an oxygen index value of about 25, and have tensile strength values of about 5000 psi at 450% elongation.

The most efficient additives for imparting flame retardancy to spandex urethanes are aromatic halides and the most effective of these are the bromide compounds. Various levels of flame retardancy were achieved, depending on the levels of additives used. Compositions were prepared and tested to meet the following specifications:

a. **31% Oxygen/69% Nitrogen at 10 psia**: These urethane compounds have tensile strengths of 1500-2000 psi and elongations of 300-450%. They contain 20-30% urethane with the remainder flame-retardant additives (hexabromobenzene in combination with trisbromochloropropyl phosphate as a flame-retardant plasticizer).

b. **70% Oxygen/30% Nitrogen at 6.2 psia**: These urethane compositions have tensile strength values of 400-900 psi, elongations of 250-400%, and oxygen index values of 75-85. They are composed of about 5% urethane, 20-30% fluorinated polymer, and 65-75% hexabromobenzene/trisbromochloropropyl phosphate.

Although it was possible with the urethanes to achieve the necessary flame retardancy, the physical properties were so inferior that serious problems would be encountered in making fabrics with the necessary recovery and strength characteristics. For these reasons a fluorocarbon elastomer compound was developed and provided better nonflammability and higher strength. The major portion of our work has been with this material and the approved product was based on a fluorocarbon elastomer.

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In the second phase of the program, carried out in 1971 and early 1972, the elastomeric fibers' physical properties were improved and a limited number of fabrics were produced from these fibers in combination with fiberglass, Nomex and PBI fibers. To achieve these results, we had to evaluate a large variety of flame-retardant additives and prepare enough of the fabrics to indicate the type of structure that would be required to obtain properties nearly equivalent to those of standard spandex fiber fabrics. During this phase, we prepared films and fibers, as well as knit structures, that met the flame-retardancy requirements and that have physical properties approaching those of spandex fabrics. We achieved equivalent physical properties by increasing the amount of elastomeric material in the fabric.

The third phase (covered in this report), carried out in 1972 and early 1973, resulted in a substantial improvement in physical properties and manufacturing techniques. Properties were especially improved when a standard curing system was replaced by a unique cure based on peroxide and maleimide. This change made the compound easier to process, and provided the elongation and strength necessary to make a satisfactory fiber. Rates of production and fiber characteristics were improved by the use of a new 1″ extruder with a longer barrel, the use of a modified die design with a larger number of orifices, the use of an improved take-up device, and improvements in collection and curing procedures.

No elastomeric fibers are now extruded commercially as uncured fibers which are then collected and cured. To do this at the required levels of production necessitated the development of very specialized handling techniques for the fibers after they came out of the extruder.

PBI fibers were selected for wrapping the elastomer fibers. Structures of power net were developed by John Somak, Inc., in cooperation with us. One of these was selected and 50 pounds of material was extruded for use in making sleep monitoring caps, and other crew equipment and spacecraft applications in the Skylab program.

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III. PROPERTIES AND COMPOUNDING

This section reviews the steps that were taken to improve the fiber strength, power, and elongation, and to make the compound more suitable for processing. In addition, compound changes were made to achieve maximum flame retardancy at the lowest possible loading of additives and to reduce the amount of smoke generated.

A. CURING SYSTEMS

Fluorinated rubbers normally are cured with a metallic oxide, which promotes the elimination of hydrogen fluoride. The resulting unsaturation provides sites for vulcanization with difunctional amines. In our prior work we investigated different combinations of metallic oxides and amines and finally selected lead oxide or magnesium oxide as the metallic oxide and Diak No. 3 (N, N'-di-cinnamylidene-1, 6-hexane-diamine as the amine).

The second system that we used was a combination of a peroxide curing system and maleimide, which is not a particularly well-known curing system for fluorinated rubbers. Table III-1 shows a comparison of the physical properties of an amine system and the maleimide cured with two different peroxide systems. Figures III-1 and III-2 show the retained strength of the three systems when they are repeatedly elongated to 50% and 100%, respectively.

TABLE III-1

PROPERTIES OF DIFFERENT CURING SYSTEMS

| Ingredients	Parts By Weight							
	95A	95B	95C	95D	96A	96B	96C	96D
Viton B	100	100	100	100	100	100	100	100
Lead Oxide	15	—	—	—	—	—	—	15
Magnesium Oxide	—	15	15	15	15	15	15	—
N-(-4-carboxy phenyl) Maleimide	4	4	4	4	4	4	4	—
Diak No. 3	—	—	—	—	—	—	—	4
Tricresyl Phosphate	—	—	—	—	—	—	—	10
Benzoyl Peroxide	4.5	4.5	—	—	—	4.5	—	—
Benzoyl Peroxide in Silicone Oil (50% by wt.)	—	—	—	—	9.0	—	—	—
Dicumyl Peroxide	—	—	4.5	—	—	—	6.75	—
2,5-Dimethyl-2,5-di(t-butyl peroxy) Hexane	—	—	—	4.5	—	—	—	—
Decabromobiphenyl	—	—	—	—	100	100	100	100
Power, psi (after two cycles)								
1. at 50% elongation	—	—	—	—	426	—	373	396
2. at 100%elongation	—	—	—	—	488	—	294	407
3. at 200% elongation	—	—	—	—	568	—	360	429
4. at 300% elongation	—	—	—	—	—	—	347	474
5. at break (elongation)	—	—	—	—	2100 (450%)	—	—	1300 (500%)

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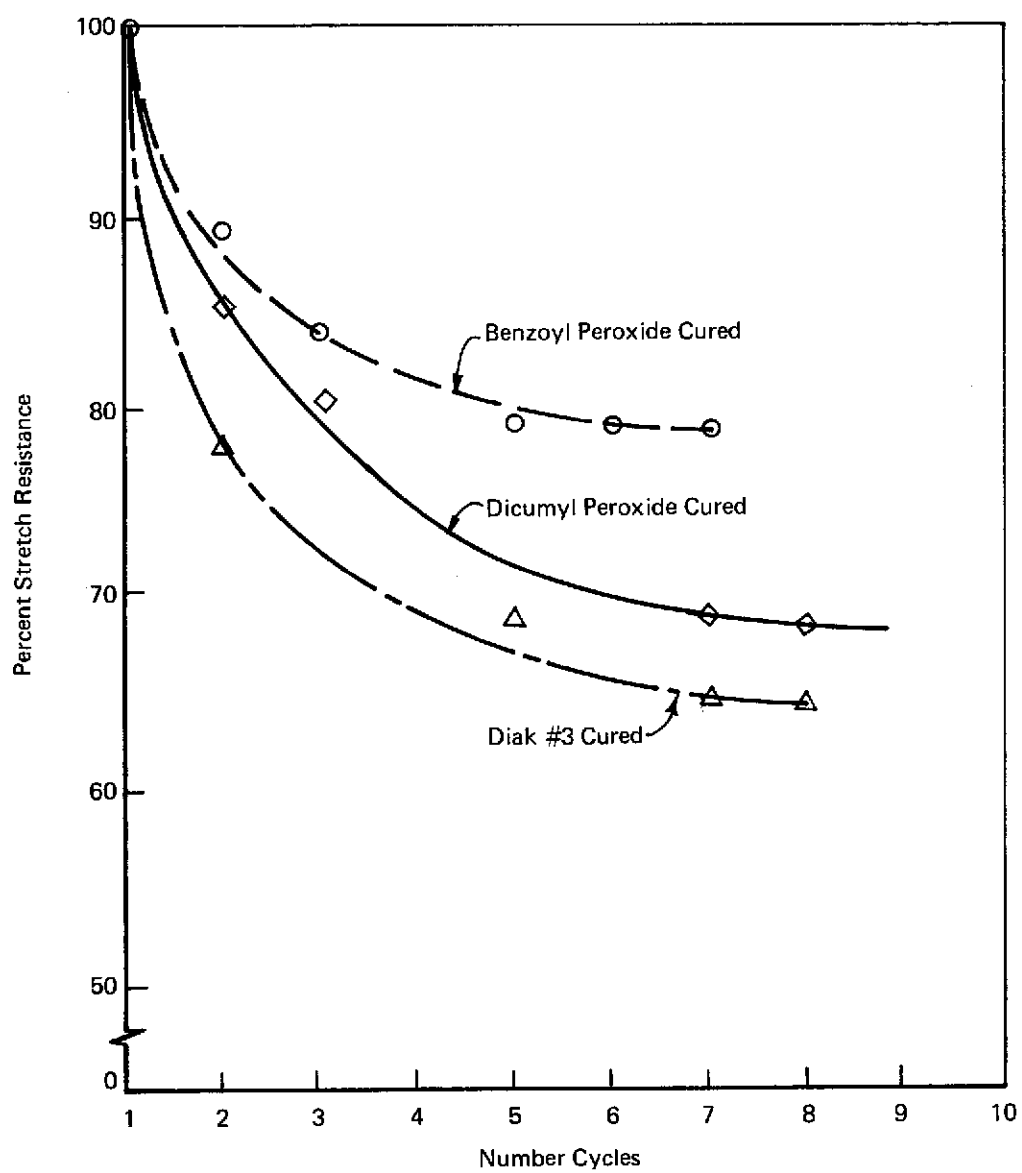
FIGURE III—1   STRETCH RESISTANCE ON CYCLING AT 50% ELONGATION
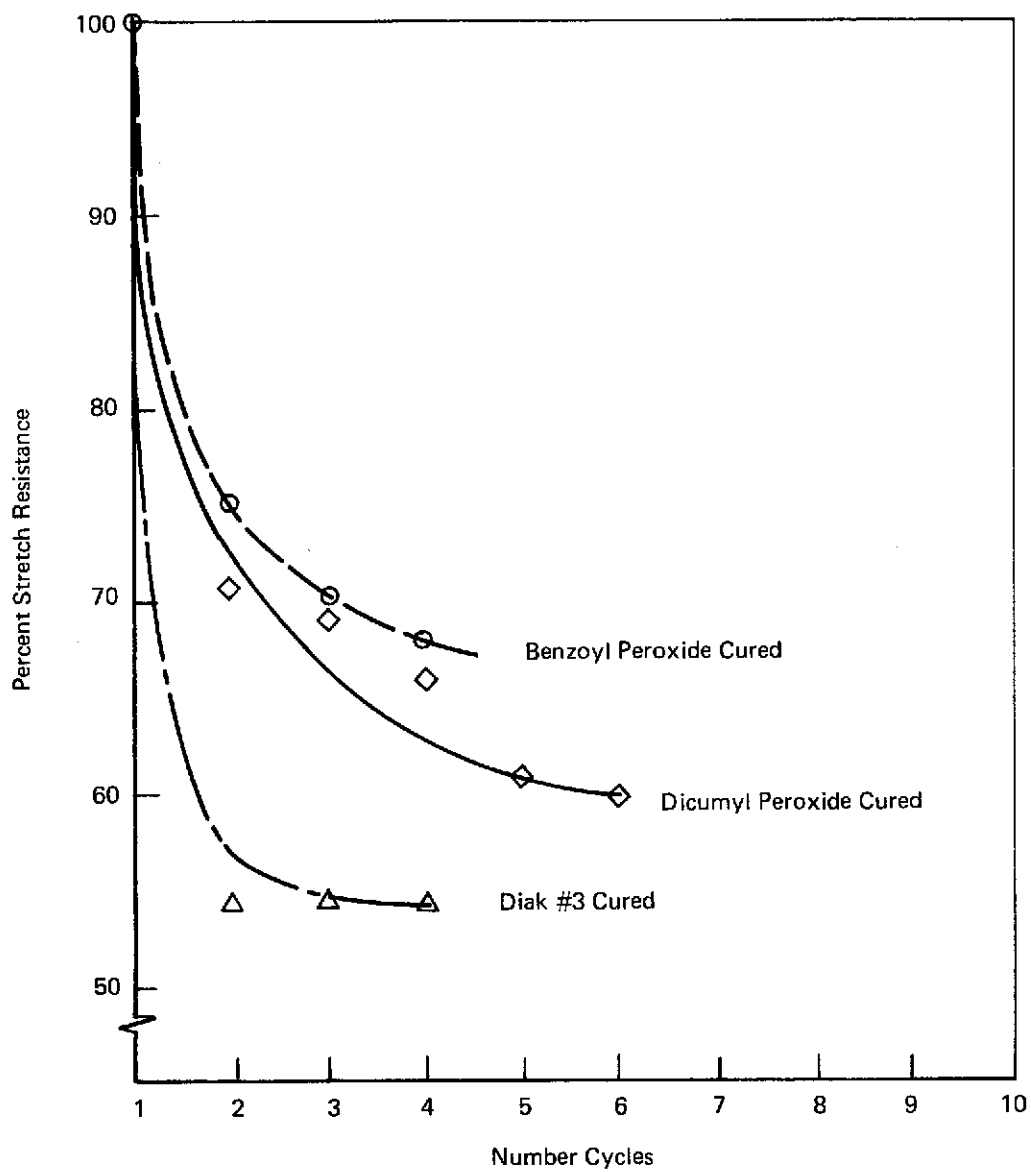
FIGURE III–2   STRETCH RESISTANCE ON CYCLING AT 100% ELONGATION

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Work was started with the peroxide curing system in September 1972, but certain portions of the data applying to plasticizers, fillers, etc., were developed on the basis of the Diak curing system. However, the conclusions apply to both systems.

B. EFFECT OF FILLER CONCENTRATION ON FIBER PROPERTIES

As the level of flame-retardant filler in the elastomeric fiber formulation increases, the strength and elongation of the fiber decreases. In many applications, however, the fiber will be embedded within nonflammable fibrous structures, and high levels of flame-retardant filler are not required. Table III-2 shows five formulations prepared with different amounts of filler and the physical properties of each.

TABLE III-2

FORMULATIONS TESTED

	16933-79A	-79B	-79C	-79D	-79E
Viton B	100 pts	100 pts	100 pts	100 pts	100 pts
Decabromobiphenyl	0	25	50	100	150
Tricresyl Phosphate*	0	2.5	5.0	10	15
Lead Oxide	15	15	15	15	15
Diak No. 3	4	4	4	4	4
Tensile Strength, psi	3000-4000	2000-3000	1500-2500	1300-1500	800-1000
Ultimate Elongation, %	690-730	500-600	500-600	350-450	400
Oxygen Index	40	63	85	100	100

* The level of tricresyl phosphate is increased as the level of decabromobiphenyl filler and flame retardant is increased to improve the elongation of the elastomeric formulation.

These formulations were extruded through a 12-hole die at a temperature of 200°F. The fibers produced were cured 16 hours at 400°F and then tested for tensile strength, ultimate elongation, and oxygen index.

The physical properties of fibers prepared from formulation 16933-79A compare favorably with those of commercially available cut rubber yarn. In addition, these fibers are self-extinguishing in air and have an LOI of 40. Consequently, these fibers may be useful in a host of commercial applications where powerful, flame-resistant elastic fibers are needed.

Fibers prepared from formulation 19633-79D have been double wrapped with treated PBI or Beta Fiberglas and knitted into a variety of fabric structures. These fabrics were tested at NASA and found to be self-extinguishing in 70% oxygen/30% nitrogen environments at 6.2 psia.

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Formulation 16933-79E has 50% more flame-retardant filler than 16933-79D. Fibers prepared from this formulation are self-extinguishing in 70% oxygen without any protective covering. This elastomer may be useful in Skylab applications such as rubber hosing, belts, and cushion where fair strength, good elongation, and excellent flame resistance are required. Flame retardancy relates directly to the weight and surface area of the material involved in the test. Thus, the formulations with lower levels of decabromobiphenyl 16933-79B and C wrapped may well pass because the wrapping forms a heat sink and holds the flame-retardant gases given off during the primary ignition on the fiber surface longer.

C. EFFECT OF PLASTICIZERS ON FIBER PROPERTIES

The lead oxide-Diak No. 3 curing system results in fibers that are difficult to extrude. Moreover, a smooth surface can be obtained only with difficulty. Finally, their elongation is lower than desirable. A minimum elongation between 350 and 400% was desirable. As the decabromobiphenyl in the formulation was increased, it was necessary to increase the tricresyl phosphate, which we had used up to this time, to between 10 and 15 parts. This resulted in an uncured fiber that was extremely soft, difficult to extrude and difficult to take up.

The objective was to make the fibers slip through the die orifices easily and thus create a minimum of back pressure and a smooth surface. For this reason, we evaluated three high-temperature stable materials as plasticizers and as die lubricants: a fluorosilicone (Dow Corning FS 1265 fluid 10,000 centistokes), an ester (Union Camp's Uniflex 330), and tricresyl phosphate.

As Table III-3 shows, the highest strength fibers were obtained with tricresyl phosphate and the lowest with Uniflex 330. Since the tensile strength of the

TABLE III-3

EFFECT OF PLASTICIZERS ON FIBER PROPERTIES

	FS 1265 Fluid	Uniflex 330	Tricresyl Phosphate	
Viton B	100	100	100	100
Lead Oxide	15	15	15	15
Diak No. 3	4	4	4	4
Decabromobiphenyl	100	100	100	100
FS 1265	10	—	—	—
Uniflex 330	—	10	—	—
Tricresyl Phosphate	—	—	10	5
Tensile Strength	1060 psi	885 psi	1440 psi	1540 psi
Elongation	440%	530%	450%	275%

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elastic fiber is of crucial concern in the manufacture of power net fabrics, the fiber that contains tricresyl phosphate (TCP) is best suited to this application. When the level of TCP was lowered to 5 phr*, fiber elongation decreased. Consequently, in our work we decided that 10 phr of TCP provided the best balance of desirable physical properties and processing characteristics when the lead oxide-Diak No. 3 cure system was used.

D. FLAME RETARDANCY

1. Flame-Retardant Additives

From our evaluation of the flame retardants we had selected decabromo-biphenyl as the most efficient flame retardant.** Since it comes in extremely fine particle size, it does not interfere with the strength characteristics significantly as some larger-particle-size flame retardants do. Decabromobiphenyl oxide is as effective a flame retardant as the decabromobiphenyl, and potentially more effective because it decomposes thermally 50° higher than the decabromo-biphenyl.

2. Metallic Oxides — Flame Retardancy

Fibers were prepared with different metallic oxides to determine their effect on flame retardancy. Fibers cured with magnesium oxide rather than lead oxide had higher strength, but the oxygen index was reduced about 10 points. This work was done with the maleimide-peroxide-metallic oxide curing systems. The lead oxide curing system gives an LOI of 50 and the magnesium oxide an LOI of 33, but the magnesium oxide has substantially higher tensile strength. (See Table III-4.)

E. SMOKE RETARDANCY

The hazard of a fire in the confines of spaceships stems not only from the flames, but also from the smoke produced. Even though fibers are self-extinguishing in an atmosphere of 70% oxygen, the material, like all organic polymers, will smoke if it is continuously exposed to a high enough heat source. Therefore, we have pursued the development of potential smoke retardants.

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* phr = parts per hundred rubber.

** Since the time the work covered in this report was completed we have found sodium aluminum sulfate to be extremely effective both in reducing smoke and in increasing the flame resistance. This work will be covered in detail in subsequent reports.

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TABLE III-4

CURING SYSTEMS

Material	16933-112A	16933-112B	16933-112C	16933-113A	16933-113B
Viton B	100	100	100	100	100
Lead Oxide	15	15	50		
Magnesium Oxide				15	
Zinc Oxide					10
Dyphos*					10
Maleimide	4	4	4	4	4
Benzoyl Peroxide	4.5	4.5	4.5	4.5	4.5
Aluminum Powder		5			
LOI	50	35	35	33	45
Tensile Strength, psi	3200			4000	
Elongation, %	500			550	

* Dibasic lead phosphite.

It has been known for some time that certain metal additives act in the vapor phase to suppress smoke formation, but a practical smoke retardant has been difficult to develop because very few metal-containing compounds exhibit the volatility required to get the metal from the solid phase into the vapor and still are heat stable enough to remain in the compound during cure.

One compound, dicyclopentadienyl iron (ferrocene), has been found to combine the necessary properties to make it an effective smoke retardant for common polymers (e.g., PVC, polystyrene, and polyurethanes) when used at a level of 0.5 to 5% by weight of polymer. To evaluate ferrocene in a compound, we prepared the compositions shown in Table III-5.

TABLE III-5

SMOKE RETARDANT MATERIALS

Ingredient	Parts By Weight	
	Formulation 86A	Formulation 86B
Viton B	100	100
Decabromobiphenyl	100	100
Lead Oxide	15	15
Tricresyl Phosphate	10	10
Diak No. 3	4	4
Ferrocene	2	1/2

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A visual comparison of smoke produced during the burning (in a 70% O_2 atmosphere) of compression molded samples of these formulations and of samples not containing ferrocene revealed no significant differences.

An examination of the press plates in which the samples were molded showed that ferrocene crystals had apparently sublimed from the rubber at the 320°F molding temperature. Since the molded samples were subsequently post-cured for 16 hours at 400°F in an air circulating oven, the ferrocene undoubtedly vaporized during this procedure.

To circumvent this problem, we incorporated a less volatile ferrocene derivative, ferrocene dicarboxylic acid, which sublimes at 200°C, in the formulation (Table III-6).

TABLE III-6

SMOKE RETARDANT MATERIALS
(Parts)

Ingredient	Amount
Viton B	100
Decabromobiphenyl	100
Lead Oxide	15
Tricresyl Phosphate	10
Diak No. 3	4
Ferrocene Dicarboxylic Acid	1/2

Once again, no visual difference was noted in the burning behavior of the "smoke retardant" and nonretardant compositions. In this case, however, the ferrocene dicarboxylic acid appeared to remain in the samples, but was just not an effective smoke retardant. To confirm this, we evaluated both ferrocene and ferrocene dicarboxylic acid in *polystyrene* at a level of 0.8% by weight of polymer.

Samples of each formulation were burned in air, and the smoke produced was vacuum-collected on preweighed glass filters. The results indicated that ferrocene dicarboxylic acid was about 20% *more* effective than ferrocene in reducing the smoke. Apparently then, in the case of the Viton, either the dicarboxylic acid form is not an effective smoke retardant, or is still too volatile to remain in the rubber sample during post-cure. We suspect the latter is true. In any event, other more effective agents were sought among the organometallic compounds based on: barium, molybdenum, strontium, tungsten, potassium, alkaline earth metals and iron oxide.

We found that if these nonvolatile agents are added directly to the flame, they catalyze the oxidation of carbonaceous materials to carbon monoxide and

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carbon dioxide and less smoke is produced. However, if these materials are incorporated directly into polymers, the lack of volatility prevents them from reaching the flame front and they are ineffective as smoke suppressants. The best material for reaching the flame front was ferrocene; it volatilizes into the vapors, but at the same time, it is too volatile to stand the cure cycle. We can cure at lower temperatures with some strength loss, but we further examined other smoke suppressants that would not volatilize at the curing temperature.

Certain additional smoke suppressants, together with the best of those evaluated in the Diak 3-metallic oxide, were prepared with the maleimide-peroxide curing system.

These compounds were prepared using the maleimide curing system with magnesium oxide and benzoyl peroxide. A less than normal amount of decabromobiphenyl was added, 80 parts versus 100 parts, so the material would burn more readily. Two and one-half parts of each of the smoke retardants were incorporated into the formulation on the mill and the sheet press cured at 300°F for 25 minutes and then post-cured in an oven at 400°F for 12 hours.

Some of the additives adversely affected the curing mechanism; others were not effective smoke reducers. However, two of the materials, zinc phenol-sulfonate and aluminum trihydrate, reduced the overall amount of smoke and changed its color from black to white. Increasing their levels further decreases smoke generation. The complete formulations are listed in Table III-7 with comments on the cure and a general rate of smoke emission. The effect of the various materials was as follows:

Ingredients	Comments
1. Aluminum Hexahydrate	good cure, smoke no change
2. Aluminum Trihydrate	good cure, some improvement
3. Cobaltic Acetyl Acetonate	poor cure, smoke no change
4. Ferrocene Dicarboxylic Acid	poor cure, smoke no change
5. Ferrocene FE55	poor cure, smoke no change
6. Magnesium Acetyl Acetonate	poor cure, smoke no change
7. Sulfur	no cure, smoke no change
8. Zinc Phenolsulfonate	good cure, less smoke

The ability of the zinc phenolsulfonate to reduce the smoke depends on the atmosphere in which it is burned. Under normal atmospheric conditions, where the oxygen content is about 20%, very little difference can be seen between the control and the sample containing the zinc phenolsulfonate. However, where the oxygen concentration is above 75%, the smoke becomes whiter than the control and significantly less smoke is emitted in the early stages of burning.

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TABLE III-7

EVALUATION OF SMOKE RETARDANTS

Ingredients	Parts By Weight											
	100-1*	100-2	100-3	100-4	100-5	100-6	100-7	100-8	100-9	100-10	100-11	100-12
Viton B	100	100	100	100	100	100	100	100	100	100·	100	100
Magnesium Oxide	15	15	15	15	15	15	15	15	15	15	15	15
N-(4-carboxy phenyl) Maleimide	4	4	4	4	4	4	4	4	4	4	4	4
Benzoyl Peroxide	9	9	9	9	9	9	9	9	9	9	9	9
Decabromobiphenyl	80	80	80	80	80	80	80	80	80	80	80	80
Zinc Phenolsulfonate									2.4	4.8	12	24
Cobaltic Acetyl Acetonate						2.4						
Ferrocene			2.4									
Ferrocene Dicarboxylic Acid				2.4								
Aluminum Trihydrate					2.4							
Sulfur		2.4										
Magnesium Acetyl Acetonate							2.4					
Aluminum Hexahydrate								2.4				
Physical Properties — See Footnote	①	②	②	②	①	②	②	①	①	①	①	②
Smoke Emission Rating 1-10**	10	10	10	10	8	10	10	10	7	6	5	4
Color of Smoke	black	black	black	black	dark gray	black	black	black	dark gray	gray	white	white

* Control formulation

** 10 is the same as control. As the number decreases from 10, emission is lower.

① No change in physical properties.
② Sample did not cure completely.

We conclude that zinc phenolsulfonate is the best smoke-retardant material.

1. Polymer Types

In order to obtain basic information on the amount of smoke given off from different types of polymers, we prepared the following series of formulations:

Elastomer Type	Cure System	Flame Retardant	Smoke Retardant
Fluorocarbon	Maleimide	Decabromobiphenyl	Zinc phenolsul- fonate
Neoprene	Magnesium oxide	Ammonium bromide	Ferrocene
Urethane	Polymeric isocyanate	Hydrated alumina	None
SBR	Standard sulfur	Ammonium bromide	Ferrocene
EPDM	Standard sulfur	Ammonium bromide	Ferrocene

The formulations of these compounds, oxygen index, and the results of the NASA burning test are shown in Tables III-8 through III-11.

a. Fluorocarbon Elastomers

Commercially available, unmodified fluoroelastomers are not satisfactory for NASA applications because these materials burn readily in 70% oxygen environments. If a flame retardant such as decabromobiphenyl is incorporated in the fluoroelastomers, elastomeric compositions which pass NASA's flammability requirements may be prepared. However, because this retardant tends to inhibit the combustion reactions, a large amount of partially oxidized soot and condensible gases is emitted from the flame-retarded fluoroelastomer when it is exposed to flame.

Initial attempts to minimize this smoke generation by incorporating zinc phenolsulfonate and other smoke retardants into the formulation were only partially successful (see Table III-8), even in an atmosphere of only 29% oxygen at 10 psia.

We have observed that when the amount of decabromobiphenyl is reduced, the tendency of the composition to smoke is also reduced. Formulations without any decabromobiphenyl but with lead oxide and peroxide maleimide curing systems exhibit a limiting oxygen index of 50 and relatively low level of smoke generation. At present, these elastomeric formulations are the best polymer systems we have investigated for NASA applications.

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TABLE III-8

FLUORINATED POLYMER (VITON)

Material	Parts By Weight			
Code #106	A	B	C	D
Viton B	100	100	100	100
Lead Oxide	15	15	15	15
Maleimide	4	4	4	4
Benzoyl Peroxide	4.5	4.5	4.5	4.5
Decabromobiphenyl	100	100	100	100
Zinc Phenolsulfonate		5.0	10	
Cure minutes @ 270°F	60	60	60	60
Post Cure @ 450°F hours				15
Oxygen Index LOI	100	95	95	60
Smoke	Medium	Low	Medium	Low

NASA Tests*

Burning Time, sec.	50	120	60	60
Burned Length, inches/sec.	1	1	1	1-1/2
Smoke Density	Heavy	Heavy	Dense	Dense
Color	White	White	White	White
Odor	Strong	Strong	Strong	Strong

* Test atmosphere 10 psia 30% O_2, 70% N_2
  Silicone ignitor

b. Neoprene

Neoprene exhibits a built-in degree of flame retardancy because it contains about 40% by weight of chlorine, which is covalently bonded to a hydrocarbon backbone. Nonetheless, unmodified neoprene will not meet the flammability requirement in 30% oxygen environments. In addition, neoprene burns with a dense black smoke, even with one of the best smoke retardants (ferrocene) incorporated in the formulation (see Table III-9).

c. Butadiene Styrene

Since butadiene styrene rubber (SBR) is the least expensive rubber, we felt there might be a possibility of using it as an extender for the more expensive rubbers. The polymer burns with a dense black smoke and burns readily in air. Excessive flame retardant levels would be necessary to pass the requirement and since the polymer is such a smoke producer, it has no practical value for NASA. Test results are given in Table III-10.

TABLE III-9

NEOPRENE

Material	Parts By Weight		
Code #108	A	B	C
Neoprene W	100	100	100
Magnesium Oxide	4	4	4
Clay	85	85	85
Hydrated Alumina (Alcoa C-333)	85	85	85
Ammonium Bromide	—	40	40
Ferrocene	—	—	4.0
Process Oil	55	55	55
Zinc Oxide	5	5	5
Titanium Dioxide	10	10	10
Stearic Acid	6	6	6
Antioxidant	2	2	2
NA-22	0.5	0.5	0.5
Cure Condition, min. @ 350°F	20	20	20
LOI	26-27	36	35
Smoke	Medium	Medium	Medium

NASA Tests*

Burning Time, sec.	Total Burn	Total Burn	Total Burn
Burned Length, inches/sec.	0.18	0.116	0.125
Smoke	Heavy	Heavy	Heavy
Density	Sooty	Sooty	Sooty
Color	Black	Black	Black
Odor**	Acid	Acid	Acid

* Test atmosphere 10 psia 30% O_2, 70% N_2
  Silicone ignitor

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TABLE III-10

BUTADIENE STYRENE (SBR)

Material	Parts By Weight		
Code #109	A	B	C
SBR 1506	150	150	150
Natural Rubber	15	15	15
Whiting	200	200	100
Clay	100	100	50
Hydrated Alumina (Alcoa C-333)	—	150	150
Process Oil	116	58	58
Ammonium Bromide	—	120	—
Dechlorane 604	—	—	120
Ferrocene	—	5	5
Zinc Oxide	12	12	12
Sodium Bicarbonate	15	15	15
Antioxidant	1.5	1.5	1.5
Stearic	15	15	15
MBTS	2.0	2.0	2.0
TMTD	2.0	2.0	2.0
DOTG	1.0	1.0	1.0
Sulfur	7.5	7.5	7.5
Cure Condition, min. @400°F	2	2	2
LOI	19	29	27
Smoke	Medium to High	Medium to High	Medium to High

NASA Tests*

Burning Time, sec.	Total Burn	Total Burn	Total Burn
Burned Length, inches/sec.	0.16	0.15	0.12
Smoke Density	Heavy	Heavy	Heavy
Color	Black	Black	Black
Odor	Strong	Strong	Strong

* Test atmosphere 10 psia 30% O_2, 70% N_2
  Silicone ignitor

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d. Ethylene Propylene

The ethylene propylene rubbers are unique in the low levels of smoke they produce on burning and in this respect are superior to any of the other polymers. The polymer burns readily in air and must be modified to meet the 30/70 oxygen/nitrogen flammability requirement. Samples submitted to NASA, modified with ammonium bromide and hydrated alumina, give an oxygen index of 28, but do not meet the NASA flammability test. Additional work is required to improve flame retardancy. (See Table III-11.)

TABLE III-11

ETHYLENE PROPYLENE TERPOLYMER (NORDEL)

Material	Parts By Weight		
Code #107	A	B	C
Nordel 1040	100	100	100
Zinc Oxide	5	5	5
Stearic Acid	10	10	10
Whiting	60	60	60
Clay	50	50	50
Hydrated Alumina (Alcoa C-333)	110	110	110
Light Process Oil	100	50	50
Ammonium Bromide	—	80	80
Sodium Bicarbonate	20	20	20
Celogen Az	0.5	0.5	0.5
MBT	0.5	0.5	0.5
Thiuram M	1.0	1.0	1.0
EPTAC 1	1.0	1.0	1.0
Tellurium Diethyl Dithiocarbamate	1.0	1.0	1.0
Ferrocene FE 55	—	—	4.0
Sulfur	4.0	4.0	4.0
Cure Condition, minutes @ 350°F	30	30	30
LOI	20-21	28	28
Smoke	Very Low	Low	Low
NASA Tests*			
Burning Time, sec.	Total Burn	Total Burn	Total Burn
Burned Length, inches/sec.	0.38	0.1	0.166
Smoke**			
Density	Heavy	Dense	Dense
Color	White	Black	Black
Odor	Strong	—	—

* Test atmosphere 10 psia 30% O_2, 70% N_2
  Silicone ignitor

** Arthur D. Little, Inc., comment. The flame and smoke on these samples are much like a candle. Light color and substantially less than most polymers.

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e. Urethane

Urethanes burn with a very light smoke but require modification to meet the 30% O_2, 70% N_2 requirement. Modification will bring the polymer up to the required level but this will increase the smoke density. Future work will be with phosphate and hydrated alumina retardants to determine whether these low-level smoke producers will give the necessary flame retardancy.

IV. EXTRUSION TECHNIQUES

The method of producing the fluorocarbon elastomer fibers utilizes extrusion techniques to produce a finished product. Physically the process is like that outlined in our report of July 1972 except that refinements were made to allow for greater production. This new technique for making fibers; — extrusion, handling, take-up and curing of the fibers — required substantial innovation to allow production of one to two pounds of continuous fiber without a break, so that it would be suitable for handling on knitting machines. In order to produce uniform long lengths of fiber, ADL purchased a new extruder and when it was on-stream could produce 25 pounds of fibers per day.

In our original extrusion work we utilized a die that produced a maximum of 12 ends, whereas the new extruder die was made to produce 24 ends of fiber at a faster rate. Figure IV-1 shows a photograph of the production line, Figure IV-2 the extruder, Figure IV-3 the die, and Figure IV-4 the take-up.

A. EXTRUDER CONDITIONS

The temperatures in the extruder that we found optimum for processing were as follows:

Zone 1	140°F
Zone 2	150°F
Die Temperature	190-200°F

B. DIE DESIGN

The die consisted of two parts: a throat section and a second section (into which the throat section fits) which contains twenty-four 14-mil diameter holes. The holes were arranged in two rows of 12 with the holes offset. (See Figure IV-3.) A screen pack was used at the head of the extruder to filter out oversized particles of material and prevent the die holes from plugging.

C. TALCING OPERATION

Since the fibers come out of the extruder in the uncured state, they must be coated with a release agent to reduce static charge. We found the best material was talcum powder. A talcing chamber which was continuously vibrated was over the head of the extruder and extended out for about a foot. This arrangement provided the best coverage of the fibers.
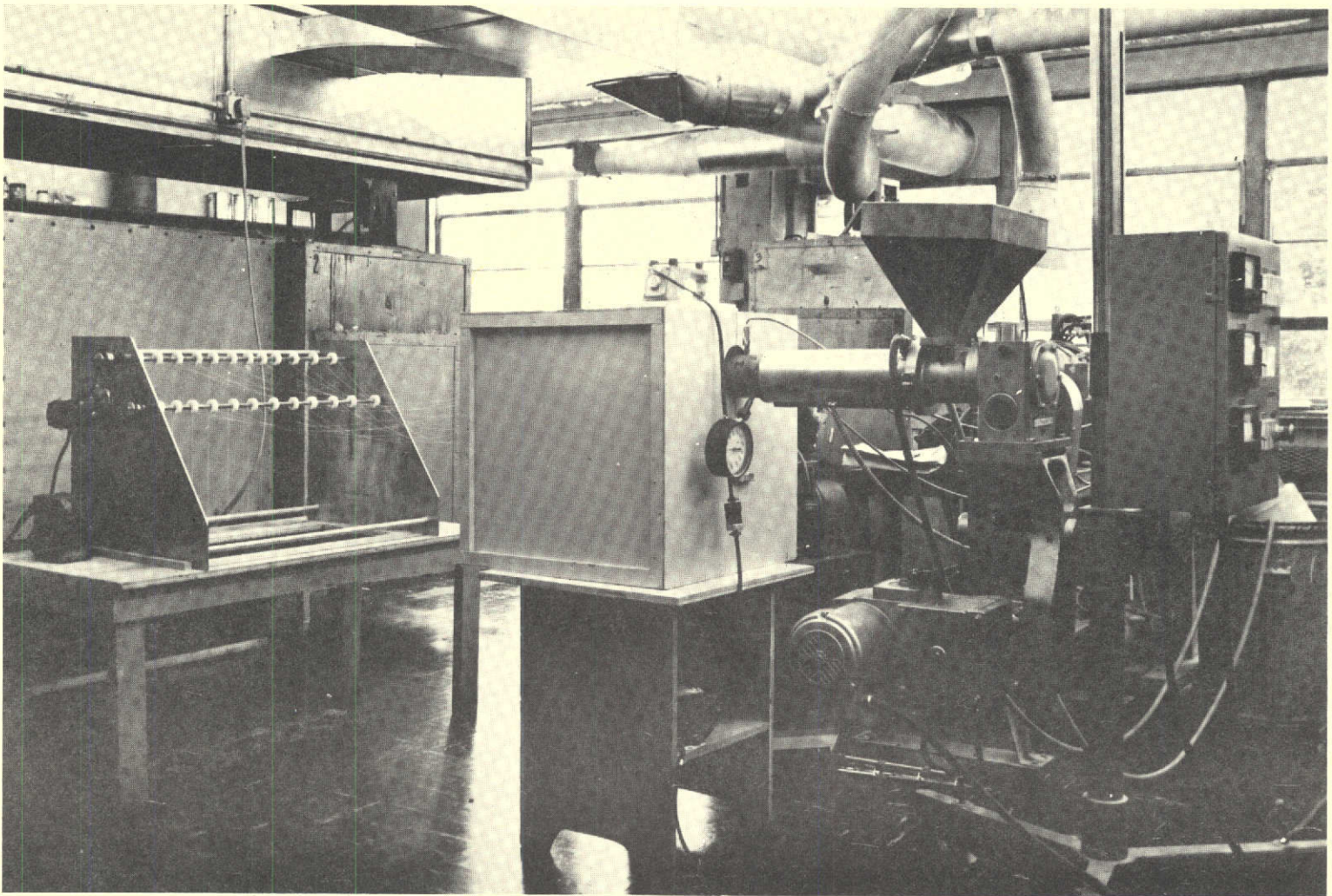
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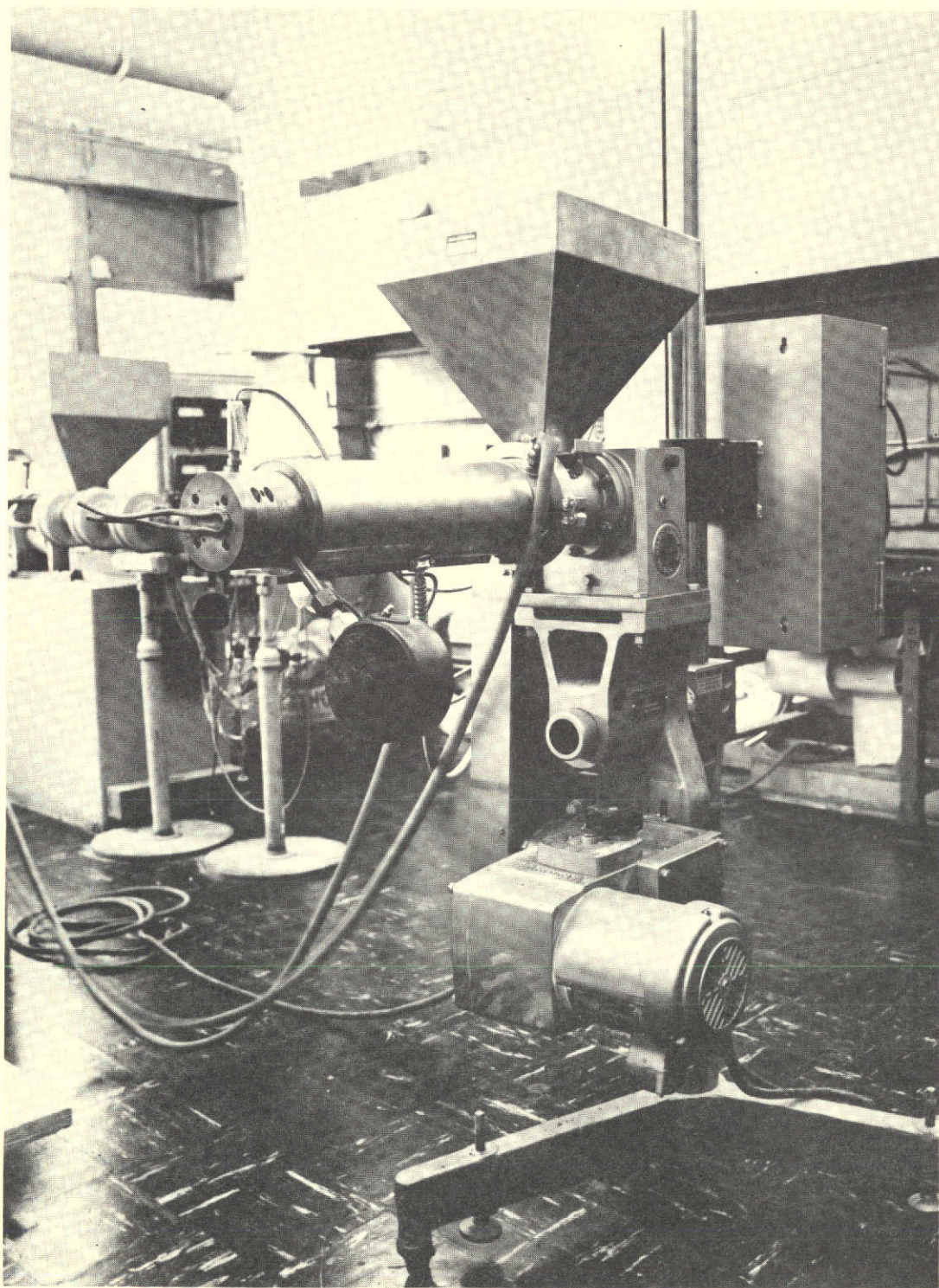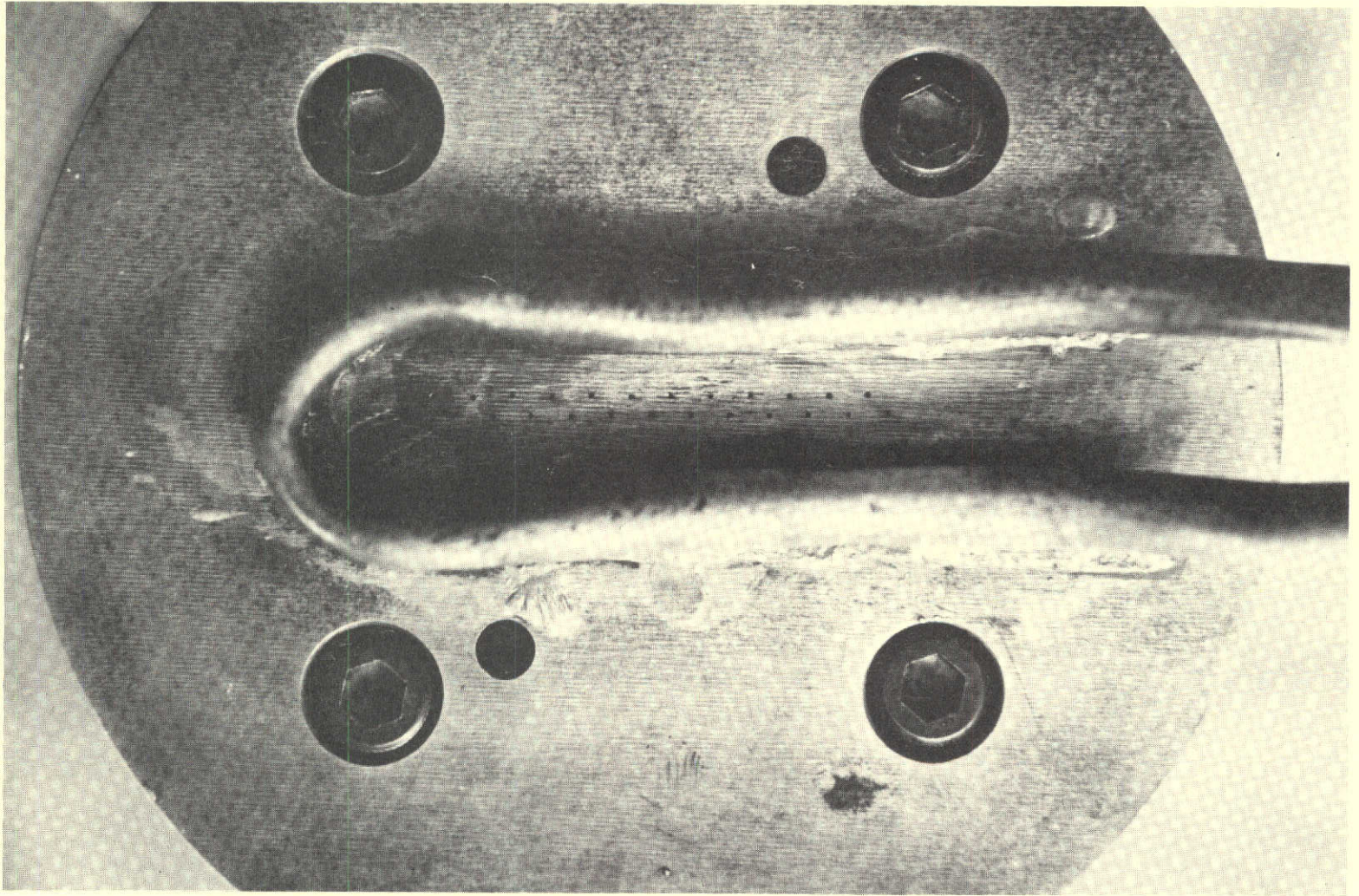FIGURE IV–1   ELASTOMERIC FIBER PRODUCTION LINE

FIGURE IV–2   EXTRUDER
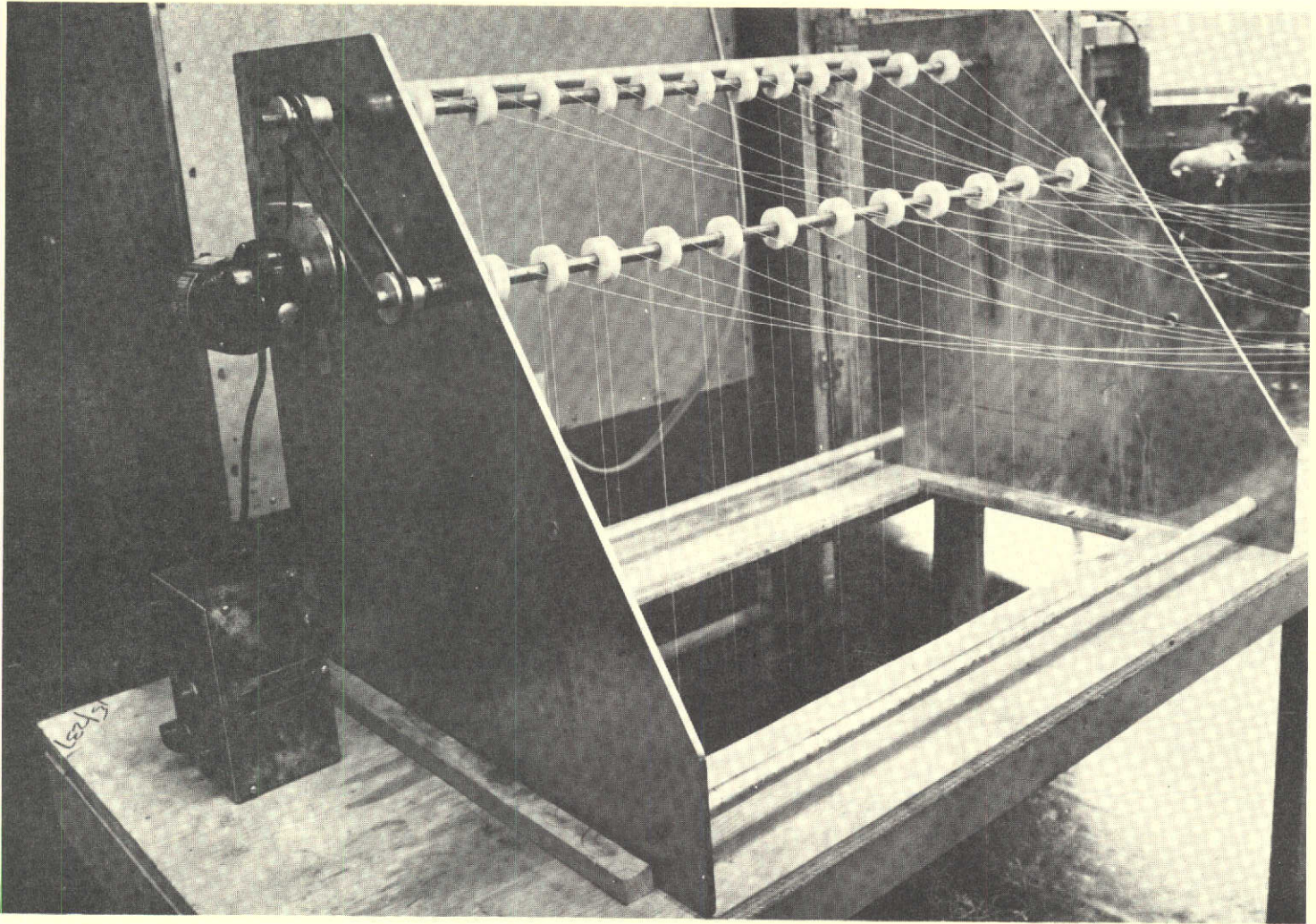
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FIGURE IV—3   24 HOLE DIE

FIGURE IV—4   FIBER TAKE-UP

D. COLLECTION AND REWIND

After passing through the talc box, the fibers were carried over rolls, as shown in Figure IV-4, and dropped into containers. The machine was run until about one pound of fiber was collected in each of the 24 containers. The fibers were then placed in an oven, cured at 400°F for 24 hours, and rewound onto spools.

E. COMPOUNDING

At the start of the program we were working with a lead oxide-Diak No. 3 type cure. Since this compound gave a low-elongation product, it was necessary to add 10 or 15 parts of tricresyl phosphate plasticizer to achieve an elongation of over 400%. During the program we tried a number of different plasticizing materials that would be compatible with the Viton B and stay in the compound during the curing cycle.

Table III-3 lists a series of materials that were tried. The fluorosilicone (Dow Corning FS 1265 fluid, 10,000 centistoke) and ester (Union Camp's Uniflex 330) and tricresyl phosphate. Of these, the tricresyl phosphate gave the highest tensile strength and a satisfactory elongation. When the level of TCP was lowered to five parts per hundred, there was a drop-off in fiber elongation. Consequently, we decided that 10 parts per hundred provided the best balance of desirable and physical properties. At this level of TCP, however, the fiber is extremely soft as it comes out of the extruder and very difficult to handle.

At this time we started working with the maleimide curing system, which had the advantage of increasing strength and elongation. With the new extruder, rates of extrusion were considerably higher than with the smaller extruder used previously but the material formed a rough surface, which necessitated finding an additive that would allow the fibers to slip through the die without hangup. Scorch was also a problem and a slower curing system was required. To improve the extrusion characteristics, we prepared a number of maleimide-peroxide cure system formulations, as shown in Table III-1, extruded fibers and tested their tensile strength, recovery, and elongation.

Magnesium oxide was used in place of lead oxide in formulations 95B-96C (Table III-1) to minimize the tendency for the formulations to cure prematurely (scorch). The flame resistance of fibers prepared with lead oxide (LOI 90) was essentially the same as those prepared with magnesium oxide (LOI 85). Formulations 95A, B, and C produced rough-textured fibers, and excessive pressure buildup in the extruder led to a termination of each of these runs. Since these formulations were found to have partially cured in the barrel so that the compound could not be forced easily through the die, we believe a processing aid

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was necessary. On the other hand, Formulation 95D, containing a liquid peroxide, was found to slip in the barrel instead of advancing at a uniform rate.

Formulations 96A and 96C were extruded into smooth, well-formed fibers without incident. However, 96B behaved like 95A-C, and could not be extruded without pressure buildup because no processing aid (silicone oil) was used. The physical properties of 96A, 96C, and the Diak-cured elastomer are listed in Table III-1 and plotted in Figures III-1 and III-2.

Formulation 96A exhibits better elastic power and greater tensile strength than Diak-cured fiber. On the other hand, Formulation 96C, which was cured with dicumyl peroxide, exhibited low elastic power to all elongations. This behavior is indicative of an incompletely cured fiber.

When the fibers were cycled (Figures III-1 and III-2), the peroxide-cured formulations recovered better than the Diak-cured elastomer.

V. CHEMICAL RESISTANCE

Tests were conducted to evaluate the resistance of the fluorocarbon elasto-
meric fiber to chemicals that the fibers might be exposed to in dry cleaning,
laundering or wearing conditions. No changes were noted in the physical prop-
erties or flame resistance.

Fiber samples, prepared according to the following formulation, were ex-
posed to chemicals that might come in contact with the fiber in normal use:

Viton A	100 pts
Decabromobiphenyl	100 pts
Tricresyl phosphate	10
Lead oxide	15
Diak No. 3	4

The exposure conditions and results of these tests are summarized in Table V-1.
After exposure, the fibers were dried at 200°C for 18 hours prior to testing.

Although the tensile strengths of the fibers vary from 1200 to 1600 psi, we
do not consider this variation is an indication of chemical attack on the fiber
because unexposed fibers exhibited tensile strengths varying over the same range.
The elongations of 400-500% are also consistent with those of unexposed fibers.

The flame resistance of the fibers was determined by measuring the oxygen
index of the samples when subjected to bottom ignition. No differences were
noted between unexposed and exposed fibers — all the samples had an oxygen
index of 100.

On the basis of this evaluation, we believe that this fiber will not be attacked
or degraded by the chemicals specified by NASA for our tests. In addition,
assuming these chemicals and the conditions of tests cover service conditions, we
also anticipate no loss in properties under use in spacecraft or in dry cleaning and
laundering.

TABLE V-1

CHEMICAL EXPOSURE TESTS

Chemical	Concentration	Temperature	Time	Tensile Strength psi	Elongation %
Soaps	Test at garment-use conditions			1350	450
Detergent "Tide"				1205	500
Perspiration:					
acid	AATCC	120°F	24 hrs.	1390	500
alkaline	Standard Solution			1340	500
Perchloroethylene	100%	Room	45 min.	1475	500
Perchloroethylene	100%	80°F	18 hrs.	1450	500
Stoddard's Solvent	100%	Room	45 min.	1510	500
Carbon Tetrachloride	100%	Room	45 min.	1280	500
Hydrochloric Acid	10%	120°F	24 hrs.	1425	450
Sulfuric Acid	10%	120°F	24 hrs.	1440	475
Sodium Hydroxide	10%	120°F	24 hrs.	1575	500
Hydrogen Peroxide	3%	120°F	24 hrs.	1280	500
Benzoic Acid	2%	212°F	1 hr.	1200	500
Ortho-Phenylphenol	2%	212°F	1 hr.	1200	500
Sodium Hypochlorite	1%	212°F	1 hr.	1325	500
Calcium Hypochlorite	1 ppm	Room	1 wk.	1260	450
Calcium Hypochlorite	3 ppm	Room	1 wk.	1270	500
Calcium Hypochlorite	9 ppm	Room	1 wk.	1230	450
Sea Water	100%	Room	1 wk.	1205	475
Sodium Perborate "Snowy" Bleach		140°F	10 hrs.	1200	500
Olive Oil	100%	100°F	2 wks.	1600	500
Mineral Oil	100%	100°F	2 wks.	1500	500
Lanolin	100%	100°F	2 wks.	1260	500
Rubber Processing Oil (Mobil Sol 55)	100%	100°F	2 wks.	1450	475

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VI. KNITTED FABRICS

The main objective of the program was to produce elastomeric fiber with high elastic memory that could be evaluated such as a sleep monitoring cap, and during the program approximately 75 pounds of fibers were prepared for knitting into various fibrous structures for Skylab applications.

Of the various knit fabrics, the most suitable was that prepared by John Somak, Inc. PBI which was used as a wrapping material was supplied by Fabric Research. Initially knit fabrics 7 yards long and about 18 inches wide were prepared and these fabrics were then fabricated by NASA into a sleep monitoring cap for further testings.

After initial testing, additional large quantities of knit fabrics were manufactured. Other fabric producers such as Prodesco could not duplicate the knit fabric structure which was selected by NASA. Thus John Somak produced the additional quantities. Fifteen sleep monitoring caps were prepared from this knit fabric for a Skylab Medical Experimental Altitude Test. They behaved satisfactorily and passed necessary qualification tests for acceptance. Figure VI-1 shows a sleep monitoring cap made of the material.

FIGURE VI–1   NASA SKYLAB M133 SLEEP MONITORING CAP

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VII. CONCLUSIONS

We have developed an elastic elastomeric fiber, production techniques, and knitting procedures to produce a power net fabric that meets the specifications for elastomeric fabrics used in space applications that require flame resistance in environments of 70% oxygen, 30% nitrogen, at 6.2 psia.

The major advances achieved during this year's program were:

a. Strength Improvement

Fiber strength about doubled over that previously achieved so tensile strength was increased from about 1200 psi to 2200 psi for the 70% O_2, 30% N_2. Fibers for use in environments of 30% oxygen, 70% nitrogen have tensile strength values of 3500 psi. This improvement was achieved by changing the curing system from amine-metal oxide to peroxide maleimide-metal oxide with the fluorinated elastomers.

b. Product Manufacture

Production procedures were improved through the use of a larger extruder with greater capacity. The use of a die to produce 24 ends, and a modified take-up, allowed the production of 25 pounds of fiber in 8 hours.

c. Power Net Fabrics

A variety of knit fabrics of different designs was prepared to obtain the desired power and recovery characteristics. It was shown that these fibers can be handled in much the same manner as spandex. However, since the fiber has somewhat lower power than spandex it is necessary to use either a larger diameter fiber or more fibers in a fabric designed to match an equivalent fabric containing "spandex."

d. Specifications

Qualification tests conducted at NASA show that fabrics made with the fiber and wrapped with PBI meet the specifications. Tests conducted at ADL show good aging characteristics in a 100% oxygen environment. No change in physical properties or flame retardancy has occurred over a 6-month period. Dry cleaning, common solvent, oils, etc., that might be encountered in use also have no detrimental effects.

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Arthur D Little, Inc.